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(54) Water repellent surface treatment with integrated primer

(57) An article is disclosed comprising a substrate of glass, plastic, metal, organic polymer coated substrates and inorganic coated substrates, wherein at least a portion of the surface of the substrate is treated with a composition comprising a mixture of perfluoroalkylalkylsilane and a completely hydrolyzable silane. The perfluoroalkylalkylsilane provides rain and soil repellency to the substrate surface, while the fully hydrolyzable silane hydrolyzes and condenses to form silica, which imparts resistance to weathering and abrasion, thus improving the durability of the rain and soil repellency properties. The method of providing such a durable rain and soil repellent surface comprises contacting the substrate surface with a composition comprising perfluoroalkylalkylsilane and fully hydrolyzable silane, and may include first depositing a layer of silica on the substrate surface, then contacting the substrate surface with a composition comprising perfluoroalkylalkylsilane and fully hydrolyzable silane.

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**Description****CROSS REFERENCE TO RELATED APPLICATION**

5 This application is a continuation-in-part of U.S. Application Serial No. 08/220,353 filed March 30, 1994, which is a continuation-in-part of U.S. Application Serial No. 07/589,235 filed September 28, 1990, now U.S. Patent No. 5,308,705, which is a continuation-in-part of Application Serial No. 07/503,587 filed April 3, 1990, which is now U.S. Patent No. 4,983,459.

**10 BACKGROUND**

The present invention relates generally to the art of surface treatment and, more particularly, to the art of producing a water repellent surface on various substrates, and most particularly to improving the durability of such water repellent surfaces.

**15 THE PRIOR ART**

European Patent Application No. 92107814.3 (Publication Number 0 513 690 A2) of Yoneda et al. describes a surface-treated substrate having at least two treated surface layers wherein the first outermost layer is obtained by treatment with a compound forming a surface having a contact angle of at least 70° against water and the second underlayer is obtained by treatment with at least one reactive silane compound selected from isocyanate silane compounds and hydrolyzable silane compounds.

U.S. Patent Nos. 4,983,459 and 4,997,684 to Franz et al. disclose an article and method respectively for providing a durable nonwetting surface on glass by treatment with a perfluoroalkylalkyl silane and a fluorinated olefin telomer.

25 In U.S. Patent No. 5,308,705 Franz et al. describe providing nonwetting surface properties to substrates other than glass by treatment with a perfluoroalkylalkyl silane and a fluorinated olefin telomer.

In U.S. Patent No. 5,328,768 Goodwin discloses a glass substrate the surface of which is treated with first a silica primer layer and second a perfluoroalkylalkyl silane.

**30 SUMMARY OF THE INVENTION**

The present invention provides a substrate surface with high water repellency and high lubricity. The durability of the water and dirt repellency of a substrate surface is improved by applying to the substrate surface a perfluoroalkylalkylsilane compound and a hydrolyzable silane compound. The hydrolyzable silane compound is a compound capable of hydrolytic condensation to form silica gel and functions as an integral primer compound. The surface treatment of the present invention provides enhanced durability to the water and dirt repellent surface without requiring a separate primer layer. High water repellency and lubricity are provided by perfluoroalkylalkylsilane. The hydrolyzable silane also provides for reactive drying of the solvent. The perfluoroalkylalkylsilane and hydrolyzable silane surface treatment of the present invention also provides enhanced abrasion resistance to the substrate surface. Increased resistance to humidity, ultraviolet radiation and mechanical abrasion are provided by the silane compound capable of hydrolytic condensation to silica gel.

**DESCRIPTION OF THE PREFERRED EMBODIMENT**

45 Durability of rain and soil repellency provided by application of a perfluoroalkylalkylsilane to a substrate surface is enhanced by mixing a silane or mixture of silanes capable of hydrolysis to silica gel with a perfluoroalkylalkylsilane prior to application. In accordance with the present invention, a mixture of a perfluoroalkylalkylsilane and silane or mixture of silanes capable of hydrolysis to silica gel is applied to the surface of glass to form a coating which is more durable than would have been formed without the silane or mixture of silanes capable of hydrolysis to silica gel.

50 Perfluoroalkylalkylsilane and hydrolyzable silane are applied to the surface of a substrate to produce the article of the present invention preferably as a colloidal suspension or solution, preferably in an aprotic solvent, preferably an alkane or mixture of alkanes, or a fluorinated solvent. The preferred solution of the present invention is applied to a substrate surface by any conventional technique such as dipping, flowing, wiping or spraying. The solvent is evaporated and the composition forms a durable, non-wetting, lubricating surface with improved abrasion resistance. The present invention provides the durability benefits of a primer without the additional step of applying a separate primer layer. The use of the completely hydrolyzable silane improves the humidity, ultraviolet light, and abrasion resistance of the silane surface treatment as measured by the Cleveland Condensing Cabinet, QUV (with FS40 or B313 lamps), and wet sled abrasion tests, indicating a longer useful product lifetime.

Preferred silanes capable of hydrolysis to silica gel have the general formula  $\text{SiX}_4$ , wherein X is a radical such as halogen, alkoxy, or acyl, preferably chloro, bromo, iodo, methoxy, ethoxy, and acetoxy. Preferred hydrolyzable silanes include tetrachlorosilane and tetraacetoxysilane.

The silanes,  $\text{SiX}_4$ , serve two functions. One is to become part of the coating and impart resistance to weathering and abrasion. Another function is to dry the solvent. Typical hydrocarbon solvents can contain 50 to 200 ppm of water. Other solvents can be much higher in water content. For example, a solvent containing 200 ppm water would have enough water present to deactivate a perfluoroalkylalkylsilane at 0.5 weight percent concentration. The completely hydrolyzable silane is capable of eliminating or reducing the water content of the solvent prior to perfluoroalkylalkylsilane addition. Otherwise, water deactivation of the perfluoroalkylalkylsilane would lead to insufficient coating deposition or 10 very poor durability.

Preferred perfluoroalkylalkylsilanes have the general formula  $\text{R}_m\text{R}'_n\text{SiX}_{4-m-n}$ , wherein R is a perfluoroalkylalkyl radical; m is typically one, n is typically zero or one, and  $m+n$  is less than 4; R' is a vinyl or an alkyl radical, preferably methyl, ethyl, vinyl or propyl; and X is preferably a radical such as halogen, acyloxy, and/or alkoxy. Preferred perfluoroalkyl moieties in the perfluoroalkylalkyl radicals range from  $\text{CF}_3$  to  $\text{C}_{30}\text{F}_{61}$ , preferably  $\text{C}_6\text{F}_{13}$  to  $\text{C}_{18}\text{F}_{37}$ , and most preferably 15  $\text{C}_8\text{F}_{17}$  to  $\text{C}_{12}\text{F}_{25}$ ; the alkyl moiety is preferably ethyl. R' is preferably methyl or ethyl. Preferred radicals for X include hydrolyzable chloro, bromo, iodo, methoxy, ethoxy and acetoxy radicals. Preferred perfluoroalkylalkylsilanes in accordance with the present invention include perfluoroalkylethyltrichlorosilane, perfluoroalkylethyltrimethoxysilane, perfluoroalkylethyltriacetoxysilane, perfluoroalkylethyl dichloro(methyl)silane and perfluoroalkylethyl diethoxy(methyl)silane.

These preferred perfluoroalkylethylsilanes appear to react with bonding sites at the substrate surface on a molecular 20 basis. Strong surface bonding of the perfluoroalkylethylsilanes produces a durable substrate surface which exhibits a high contact angle with a drop of water, indicating high water repellency.

Suitable solvents include isopropanol, ethanol, hexane, heptane, mineral spirits, acetone, toluene and naphtha. Preferred solvents are alkanes or halogenated hydrocarbon solvents such as trichlorotrifluoroethane, and methylene 25 chloride, and perfluorinated organic compounds such as perfluorocarbons. Concentrations of about 0.005 to 50, preferably about 0.05 to 5, percent of silane are preferred. The solvent is preferably evaporated simply by drying in air at ambient temperature, or may be removed by wiping. The silanes may also be crosslinked to form a more durable coating. Preferably, curing is accomplished by heating the silane treated surface. Typically, curing temperatures of at least 150°F (about 66°C) are preferred, particularly above 200°F (about 93°C). A cure cycle of about 200°F (about 93°C) for about 30 minutes is suitable. Higher temperatures and shorter heating times may be more efficient. A cure cycle of 2 to 5 minutes at 400 to 500°F (about 204 to 260°C) may be preferred, particularly about 3 minutes at about 470°F (about 243°C). The substrate surfaces may, in the alternative, be contacted with perfluoroalkylalkylsilane in vapor form.

The contact angles recited herein are measured by the sessile drop method using a modified captive bubble indicator manufactured by Lord Manufacturing, Inc., equipped with Gaertner Scientific goniometer optics. The surface to be measured is placed in a horizontal position, facing upward, in front of a light source. A drop of water is placed on top of the 35 surface in front of the light source so that the profile of the sessile drop can be viewed and the contact angle measured through the goniometer telescope equipped with circular protractor graduation.

Weathering chambers include the Cleveland Condensing Cabinet (CCC) and QUV Tester (products of The Q-Panel Company, Cleveland, OH). The CCC chamber was operated at a vapor temperature of 140°F (60°C) in an indoor ambient environment which resulted in constant water condensation on the test surface. The QUV Tester is operated with cycles 40 of 8 hours UV (either B313 or FS40 lamps) at black panel temperature of 65-70°C and 4 hours condensing humidity at 50°C.

The present invention will be further understood from the descriptions of specific examples which follow.

#### EXAMPLE I

45 A solution was prepared by mixing one gram of tetrachlorosilane and one gram of perfluoroalkylalkylsilane in 40 grams of trichlorotrifluoroethane (Freon® TF solvent, a product of DuPont). The perfluoroalkylalkylsilane comprised perfluoroalkylethyltrichlorosilanes, wherein the perfluoroalkyl moieties comprised primarily  $\text{C}_6\text{F}_{13}$  to  $\text{C}_{18}\text{F}_{37}$ . For comparison, a control solution was mixed without the tetrachlorosilane. The solutions were applied to the atmosphere surface 50 of 3.9 millimeter thick Solex® float glass (product of PPG Industries, Inc.) with a cotton pad. Coupons were cured at 200°F (93°C) for one hour. The excess silane was removed from the glass surfaces by solvent washing. Coupons were weathered in the CCC and QUV-FS40 weathering cabinets. Coating efficiency was measured by the contact angle of a sessile drop of water. The results are shown in the following table.

Table I

CCC			QUV-FS40		
Hours	Primer	No Primer	Hours	Primer	No Primer
0	105°	105°	0	107°	106°
496	102°	87°	319	106°	102°
927	67°	60°	1332	91°	89°
1669	49°	40°	2115	83°	79°
			2498	78°	70°
			2943	72°	57°

EXAMPLE II

Four solutions were prepared, each of which was 0.5 percent by weight perfluorohexylethyltrichlorosilane in Isopar L solvent (product of Exxon), a mixture of alkanes. The solutions had tetrachlorosilane concentrations of 0.0, 0.2, 0.45, and 0.79 percent by weight. The order of addition was Isopar L, tetrachlorosilane and perfluoroalkylethyltrichlorosilane to utilize the reactive drying of the solvent by the hydrolyzable tetrachlorosilane. These four solutions were coated on the tin surface of coupons of 0.182 inch (4.6 millimeter) thick clear float glass. Samples were tested in the CCC chamber. Coating efficiency was measured by the contact angle of a sessile drop of water. It can be seen in the following table that increasing the concentration of hydrolyzable silane within this range improves the durability of the perfluoroalkylsilane surface treatment.

Table II

Hours	CCC Contact Angle (°)			
	Primer Concentration (Percent by Weight)			
	0	0.2	0.45	0.79
0	115	115	114	114
122	81	89	105	105
284	54	65	77	81
475	36	44	58	69
642	—	—	—	47

EXAMPLE III

Four solutions were prepared, each of which was 2.5 percent by weight of the perfluoroalkylethyltrichlorosilane described in Example I and 2.5 percent by weight perfluoroalkylethylene in Fluorinert® FC-77 solvent (a product of 3M). The solutions had tetrachlorosilane concentrations of 0.0, 1.0, 2.0 and 5.0 percent by weight. These four solutions were coated on the tin surface of coupons of 0.187 inch (4.7 millimeter) thick clear float glass. Coupons were cured at 300°F (149°C) for 15 minutes. Samples were tested in the CCC and QUVB-313 chambers. Coating efficiency was measured by contact angle of a sessile drop of water. Results are given in the following tables.

Table IIIA

Hours	CCC Contact Angle (°)			
	Primer Concentration (Percent by Weight)			
	0	1.0	2.0	5.0
0	113	113	115	114
162	95	109	114	112
348	73	81	98	93
684	31	41	43	34

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Table IIIB

Hours	QUVB-313 Contact Angle (°)			
	Primer Concentration (Percent by Weight)			
	0	1.0	2.0	5.0
0	113	114	117	116
566	107	111	111	109
1375	82	95	95	87
2095	72	80	84	71

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EXAMPLE IV

Solutions were prepared comprising 0.5 percent by weight perfluoroalkylethyltrichlorosilane with and without 0.5 percent by weight tetrachlorosilane in Isopar L solvent. Three perfluoroalkylethyltrichlorosilanes were employed: 1H,1H,2H,2H-tridecafluoroctyltrichlorosilane ("octyl"), 1H,1H,2H,2H-heptadecafluorodecyltrichlorosilane ("decyl"), or a mixture of perfluoroalkylethyltrichlorosilanes described in Example I. Tempered Solex® glass coupons and clear float glass coupons that had undergone a heat treatment which simulates a bending cycle (without bending significantly) were used in this study. The Solex glass was 0.157 inch (4 millimeters) thick, the clear float was 0.090 inch (2.3 millimeters) thick, and the tin surfaces were treated. Samples were tested in the QUVB-313 chamber and on a Wet Sled Abrader (Sheen Instruments LTD, Model 903). The Wet Sled Abrader was custom modified with an aluminum block which held two automotive windshield wiper blades. The wet sled abrasion test thus configured has an unusually high pressure wiper arm loading and is done partially wet and partially dry. These wiper strokes are much more severe than normally used in vehicles. Coating efficiency was measured by the contact angle of a sessile drop of water. The plus sign "+" refers to the presence of tetrachlorosilane in the coating formulations in the following tables.

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Table IVA

Hours	QUVB-313 Contact Angle (°)					
	octyl	octyl+	decyl	decyl+	mix	mix+
0	116	112	111	115	111	118
163	102	105	87	112	102	116
352	95	95	84	107	100	111
496	82	88	74	102	89	106
659	79	80	66	93	82	99
827	70	85	60	89	82	103

Table IVB

Cycles	Wet Sled Abrasion Contact Angle (°)					
	octyl	octyl+	decyl	decyl+	mix	mix+
0	113	117	111	116	115	117
200*	86	104	79	108	86	108
600*	52	99	78	106	79	105
5000	35	84	47	91	82	92

\*These data (at 200 and 600 cycles) were obtained with a slurry of 0.5 percent by weight Hi-Sil® 233 synthetic precipitated silica in water. The data for 5000 cycles were obtained using deionized water only.

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#### EXAMPLE V

A control solution was prepared by mixing 95 grams of FC-77 solvent, 2.5 grams of perfluoroalkylethyltrichlorosilanes (perfluoroalkyl = C<sub>6</sub>F<sub>13</sub> to C<sub>18</sub>F<sub>37</sub>), and 2.5 grams of perfluoroalkylethylene. A primer-containing solution was prepared by mixing 188 grams of FC-77 solvent, 5 grams of perfluoroalkylethyltrichlorosilanes, 5.0 grams of perfluoroalkylethylene (perfluoroalkyl = C<sub>6</sub>F<sub>13</sub> to C<sub>18</sub>F<sub>37</sub>), and 2 grams of tetrachlorosilane. A primer only solution was prepared from 198.4 grams of FC-77 solvent and 1.6 grams of tetrachlorosilane. These solutions were applied to the tin surface of 4.9 millimeter thick clear float glass with a cotton pad. Selected coupons were coated with primer solution prior to coating with either control solution or the solution containing perfluoroalkylalkylsilane and tetrachlorosilane. Coupons were cured at 300°F (149°C) for 15 minutes. The excess silane was removed from the glass surfaces by solvent washing. Coupons were weathered in the CCC. Coating efficiency was measured by the contact angle of a sessile drop of water.

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Table V

Hours	CCC Contact Angle (°)			
	No primer layer		Primer layer	
	No integral primer	Integral primer	No integral primer	Integral primer
0	114	114	113	114
232	116	116	117	115
398	100	110	109	110
590	49	78	75	86
918	29	39	31	41

The solution containing a silane hydrolyzable to silica led to more durable coatings whether or not the glass was preprimed with a silica layer separately with a solution of a hydrolyzable silane.

The above examples are offered to illustrate the present invention. Various perfluoroalkylalkylsilanes, hydrolyzable silanes, solvents and concentrations may be applied by any conventional technique, and optimally cured at suitable temperatures for adequate times to provide durable non-wetting surfaces to any of a variety of glass and plastic substrates, as well as other inorganic surfaces such as metals, ceramics, enamels, and metal or metal oxide films. The treated substrates of the present invention are especially suitable in automobile and aircraft parts, as well as in building components.

### Claims

1. An article comprising a substrate at least a portion of the surface of which is treated with a composition comprising a mixture of perfluoroalkylalkylsilane and completely hydrolyzable silane wherein the substrate is selected from the group consisting of glass, plastics, metals, organic polymer coated substrates and inorganic coated substrates.
2. An article according to claim 1, wherein said perfluoroalkylalkylsilane is selected from compounds having the general formula  $R_mR'_nSiX_{4-m-n}$ , wherein R is a perfluoroalkylalkyl radical, R' is a vinyl or an alkyl radical, m+n is less than 4, and X is selected from the group consisting of halogen, alkoxy and acyl radicals.
3. An article according to claim 2, wherein the perfluoroalkyl moiety of said perfluoroalkylalkyl radical is selected from the group consisting of  $CF_3$  to  $C_{30}F_{61}$ .
4. An article according to claim 3, wherein said perfluoroalkyl moiety is selected from the group consisting of  $C_6F_{13}$  to  $C_{18}F_{37}$ .
5. An article according to claim 4, wherein said perfluoroalkyl moiety is selected from the group consisting of  $C_8F_{17}$  to  $C_{12}F_{25}$ .
6. An article according to claim 2, wherein R' is selected from the group consisting of methyl, ethyl, vinyl and propyl.
7. An article according to claim 3, wherein X is selected from the group consisting of chloro, bromo, iodo, methoxy, ethoxy and acetoxy.
8. An article according to claim 2, wherein said perfluoroalkylalkylsilane is selected from the group consisting of perfluoroalkylethyltrichlorosilane, perfluoroalkylethyltrimethoxysilane, perfluoroalkylethyltriacetoxysilane, perfluoroalkylethyl dichloro(methyl)silane and perfluoroalkylethyl diethoxy(methyl)silane.
9. An article according to claim 8, wherein said composition further comprises a fluorinated olefin.
10. An article according to claim 1, wherein said completely hydrolyzable silane is selected from the group consisting of silanes having the general formula  $SiX_4$ , wherein X is selected from the group consisting of halogen, alkoxy and acyl radicals.

11. A method of producing a non-wetting surface on a substrate comprising contacting a surface with a composition comprising a mixture of perfluoroalkylalkylsilane and completely hydrolyzable silane wherein said substrate is selected from the group consisting of glass, plastics, metals, organic polymer coated substrates and inorganic coated substrates.

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12. A method according to claim 11, wherein said perfluoroalkylalkylsilane is selected from compounds having the general formula  $R_mR'_nSiX_{4-m-n}$  wherein R is a perfluoroalkylalkyl radical, R' is a vinyl or an alkyl radical, m+n is less than 4, and X is a radical selected from the group consisting of halogen, alkoxy and acyl radicals.

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13. A method according to claim 12, wherein the perfluoroalkyl moiety of said perfluoroalkylalkyl radical is selected from the group consisting of  $CF_3$  to  $C_{30}F_{61}$ .

14. A method according to claim 13, wherein said perfluoroalkyl moiety is selected from the group consisting of  $C_6F_{13}$  to  $C_{18}F_{37}$ .

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15. A method according to claim 14, wherein said perfluoroalkyl moiety is selected from the group consisting of  $C_8F_{17}$  to  $C_{12}F_{25}$ .

16. A method according to claim 12, wherein R' is selected from the group consisting of methyl, ethyl, vinyl and propyl.

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17. A method according to claim 12, wherein X is selected from the group consisting of chloro, bromo, iodo, methoxy, ethoxy and acetoxy.

18. A method according to claim 11, wherein said composition further comprises a fluorinated olefin.

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19. A method according to claim 11, wherein the hydrolyzable silane is selected from the group consisting of silanes having the general formula  $SiX_4$ , wherein X is selected from the group consisting of halogen, alkoxy and acyl radicals.

20. A method according to claim 11, wherein the substrate surface is first primed with a layer of silica.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 95 11 9467

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
X	EP-A-0 548 775 (CENTRAL GLASS COMPANY LIMITED) 30 June 1993 * page 2, line 34 - page 3, line 38 *	1-8, 10-17,19	C03C17/30 C03C17/00 C09K3/18						
Y	---	9,18,20							
X	EP-A-0 513 727 (TOYOTY JIDOSHI KABUSHIKI KAISHA) 19 November 1992 * page 3, line 23 - line 30 * * page 5, line 1 - line 23 *	1-8, 10-17,19							
Y	---	9,18,20							
X	DE-A-42 18 657 (NISSAN MOTOR CO., LTD.) 10 December 1992 * page 2, line 30 - page 3, line 52 *	1-8, 10-17,19							
Y	---	9,18,20							
Y	EP-A-0 545 201 (PPG INDUSTRIES, INC.) 9 June 1993 * page 2, line 36 - line 39 * * page 3, line 1 - line 7 * & US-A-5 328 768	9,18,20							
D	-----		TECHNICAL FIELDS SEARCHED (Int.Cl.6) C03C						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 33%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>29 March 1996</td> <td>Van Bommel, L</td> </tr> </table> <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	29 March 1996	Van Bommel, L
Place of search	Date of completion of the search	Examiner							
THE HAGUE	29 March 1996	Van Bommel, L							